



Short communication

Facile preparation of porous FeF_3 nanospheres as cathode materials for rechargeable lithium-ion batteries

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H I G H L I G H T S

- Porous FeF_3 nanospheres were prepared using solvent exchange for the first time.
- The porous FeF_3 nanospheres show good rate capability.
- The porous FeF_3 nanospheres exhibit excellent cycle stability.

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In this communication, for the first time, we demonstrate the fast and facile preparation of porous FeF_3 nanospheres using solvent exchange from FeF_3 aqueous solution to ethanol. We further demonstrate the use of such FeF_3 nanospheres as cathode materials for rechargeable lithium-ion batteries with good rate capability and cycling performance.

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1. Introduction

The high energy density of rechargeable lithium-ion batteries (LIBs) has transformed portable electronics and will play a key role in the electrification of transport [1]. To this end, it is very currently needed to make great improvements in performance and safety, which is mainly limited by electrode materials, especially the cathode side [2]. Following the pioneering work of Poizot et al. that metal oxides can store more than one Li ion per transition metal atom through conversion reaction [3], significant effort has been put into various conversion reaction compounds, such as metal

nitrides, sulfides, fluorides, and oxides, etc [4]. Unfortunately, most of the conversion reaction compounds studied were anode materials. As a result, the development of conversion-based cathode materials with high capacity is of utmost importance.

Recently, metal fluorides with metallic cations in high oxidation states and a strong ionic character of the M–F bonds have been widely investigated due to their high theoretical energy densities and are considered as next-generation cathode materials for LIBs [4–8]. Among them, FeF_3 has attracted much attention thanks to their low cost and low toxicity. However, its application in LIBs is greatly hindered by its poor power performance, which is a result of the low conductivity of FeF_3 and slow diffusion of lithium ions in FeF_3 . The low conductivity issue can be solved by conductive coatings or introducing conductive additives [9–13]. Size reduction to nanoscale dimension can effectively solve the kinetic problems of lithium ions [14]. The use of porous structures consisting of small nanoparticles as electrode materials has an obvious advantage of

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facilitating the transport and infiltration of electrolyte, thereby offering sufficient contact interface between active materials and electrolyte. Indeed, a recent study has shown that macroporous FeF_3 structures fabricated by the colloidal crystal templating technique exhibit superior rate performance [15]. However, the preparation process is complex and very time-consuming. We report here a fast and facile preparation of porous FeF_3 nanospheres consisting of small FeF_3 nanoparticles using solvent exchange from FeF_3 aqueous solution to ethanol for the first time. As a cathode material, the as-obtained FeF_3 nanospheres show a high discharge capacity up to 193 mA h g^{-1} in a voltage range of 1.7–4.0 V at a current density of 50 mA g^{-1} and a good rate capability of 118 mA h g^{-1} at a high current density of 1000 mA g^{-1} .

2. Experimental

2.1. Materials

NaOH was purchased from Aladdin Ltd. (Shanghai, China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, HF (40%) and absolute ethanol were purchased from Beijing Chemical Corp. The water used throughout all experiments was purified through a Millipore system.

2.2. Synthesis of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$

$\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ was synthesized according to the previous method [13]. Firstly, 100 mL 1 M FeCl_3 solution was added into the 10% excess mass of stoichiometric NaOH solution (1 M) with violently stirring for 20 min and the resulted $\text{Fe}(\text{OH})_3$ precipitates were aged for 12 h, then the precipitates were washed and separated by filtration. Secondly, excessive HF solution was added to the above precipitates in a sealed PTFE bottle with continued stirring for 12 h at 70°C . Finally, the unreacted HF and water were eliminated by heating in air and the residue was dried at 80°C for 12 h in a vacuum drying oven. The as-prepared $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in water (50 mM) for further use.

2.3. Synthesis of FeF_3 nanospheres

In a typical experiment, 50 mL of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ aqueous solution was added into 200 mL of ethanol drop by drop at room temperature under stirring. A large quantity of yellow precipitate was observed with several minutes. The precipitate was then collected by centrifugation (5000 rpm, 5 min) and further washed them with ethanol several times to obtain FeF_3 nanospheres. The $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nanospheres were dried under vacuum for 12 h and further heated

at a ramp of 1°C min^{-1} from room temperature to 150°C , kept at this temperature for 12 h and cooled to room temperature naturally in Ar atmosphere in the whole process to obtain FeF_3 nanospheres.

2.4. Electron microscopy characterizations

Scanning electron microscopy (SEM) measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating applied potential of 20 kV. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscope (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) data were recorded on a Rigaku D/MAX 2550 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449 F3 Simultaneous TGA Instrument in flowing Ar atmosphere.

2.5. Electrodes preparation and electrochemical measurements

The electrodes were prepared by mixing active materials (70 wt %), acetylene black (20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP). After the above slurries were uniformly spread onto an aluminum foil, the electrodes were dried at 120°C in vacuum for 12 h. Then the electrodes were pressed and cut into disks before transferring into an Argon-filled glove box. Coin cells (CR2025) were assembled using lithium metal as the counter electrode, Celgard 2400 membrane as the separator and LiPF_6 (1 M) in ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC, 1:1:1 vol%) as the electrolyte. The galvanostatic charge–discharge tests were carried out on a Land Battery Measurement System (Land, China).

3. Results and discussion

Fig. 1A shows the SEM image of the products thus obtained, indicating the formation of hollow $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nanospheres with diameter ranging from 70 to 100 nm. The hollow nature is further supported by the corresponding TEM image, as shown in Fig. 1B. The high-magnification TEM image of one single nanosphere further reveals it is porous structure consisting of smaller nanoparticles about several nanometers in size (Fig. 1B, inset).

The $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nanospheres were heat-treated in Ar atmosphere to obtain FeF_3 nanospheres. Fig. 2A shows the TEM image of the heat-treated products. It is found that heat treatment led to nanosphere with decreased size, but its porous structure was still preserved (inset). Fig. 2B shows the XRD patterns of the samples

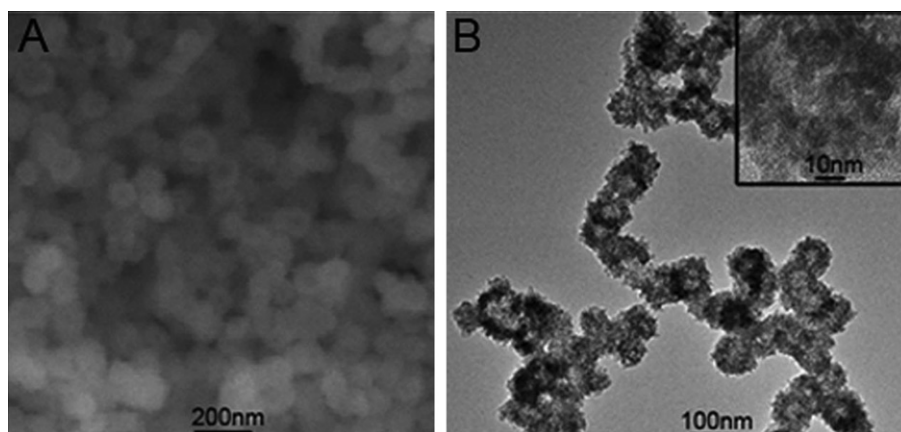


Fig. 1. SEM (A) and TEM (B) image of the products thus obtained. Inset: a high-magnification TEM image of one single nanosphere.

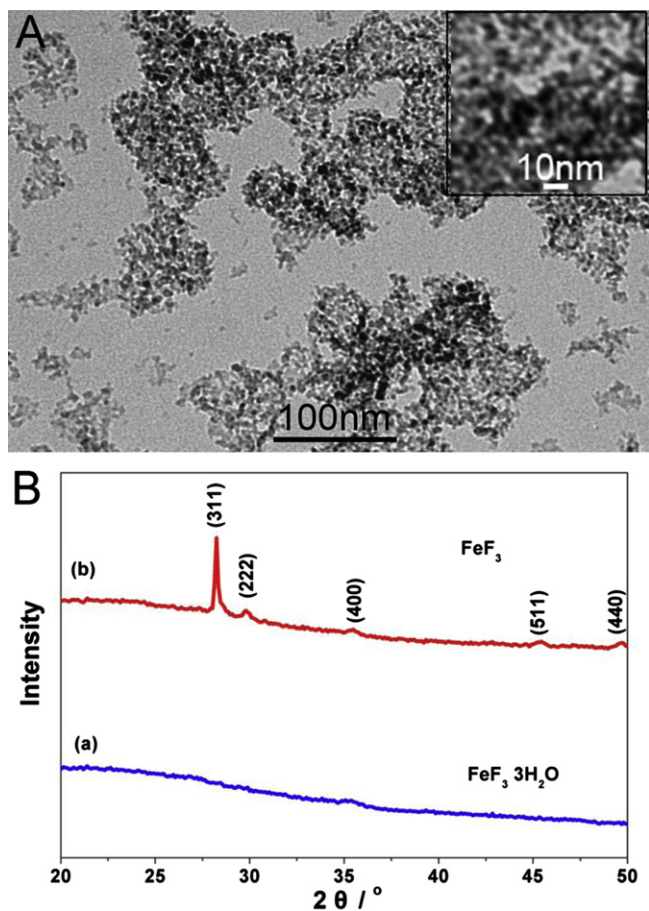


Fig. 2. TEM image of FeF₃ nanospheres (A) and XRD patterns of FeF₃·3H₂O and FeF₃ nanospheres (B).

before and after heat treatment, showing that the FeF₃·3H₂O nanospheres were amorphous and converted to crystalline FeF₃ (JCPDS 38–1305) after heat treatment. The water content in the final product evaluated by TGA was about 24%, as shown in Fig. 3.

Coin cells with a metallic Li counter electrode were assembled and galvanostatic charge/discharge technique was employed to evaluate the electrochemical performance of the product at room temperature. Because of the poor reversibility of the conversion reaction below 1.5 V [15,16], the galvanostatic charge–discharge

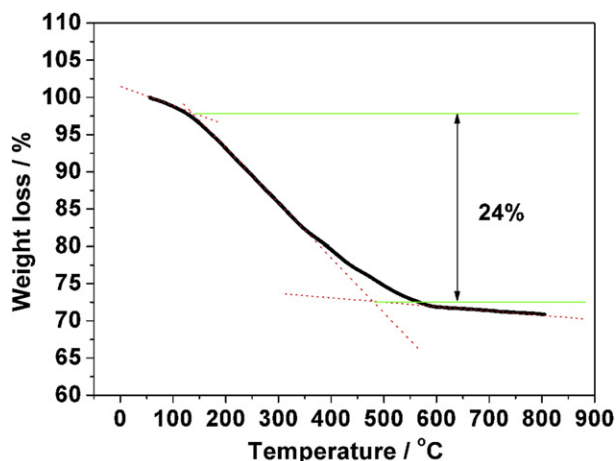


Fig. 3. TGA curves of the FeF₃ nanospheres thus obtained.

process was performed in the voltage range of 1.7–4.0 V. Fig. 4A shows the charge–discharge voltage profiles of FeF₃ nanospheres at a current density of 50 mA g^{−1}. The initial discharge capacity of the FeF₃ nanospheres can reach 222 mA h g^{−1}, with a corresponding charge capacity of 201 mA h g^{−1}. This leads to an irreversible capacity loss of about 10%. In the second cycle, a lower discharge capacity of 193 mA h g^{−1} and a charge capacity of 193 mA h g^{−1} can be reached, leading to a much higher Coulombic efficiency of 100%. This value is nearly maintained in the third cycle, showing that the irreversible loss is diminishing rapidly upon cycling. Fig. 4B shows the cycling performance of the FeF₃ nanospheres at different

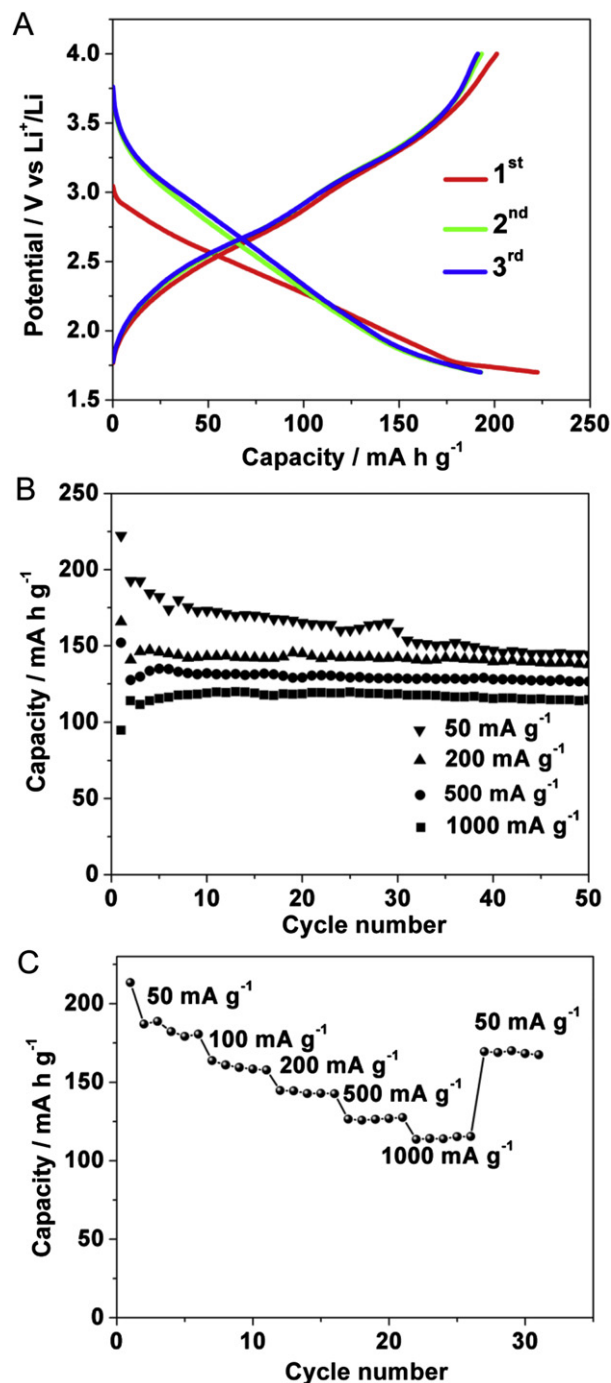


Fig. 4. Charge–discharge curves at 50 mA g^{−1} (A), cycling stability at different current densities (B) and rate capability (C) of FeF₃ nanospheres in a voltage range of 1.7–4.0 V.

current densities. The sample demonstrates good cyclic capacity retention at each current density. At the end of 50 charge–discharge cycles, a reversible capacity of 144 mA h g^{-1} can be retained at a current density of 50 mA g^{-1} . When the current density is increased to 200 mA g^{-1} , a capacity of 138 mA h g^{-1} can be delivered. Even at a large current density of 1000 mA g^{-1} , a capacity of 115 mA h g^{-1} can still be retained, implying that the lithium diffusion is highly efficient in the present FeF_3 nanospheres. The rate capability of the sample is further evaluated by charging/discharging at various current densities from 50 mA g^{-1} to 1000 mA g^{-1} (Fig. 4C). It is clear that the sample shows excellent cyclic capacity retention at each rate. It delivers a rate capacity of ca. 180 mA h g^{-1} when first cycled at 50 mA g^{-1} for 5 cycles, 143 mA h g^{-1} at 200 mA g^{-1} , and 127 mA h g^{-1} at 500 mA g^{-1} . Remarkably, a reversible capacity of 115 mA h g^{-1} can be sustained at the highest current density of 1000 mA g^{-1} , further proving the efficient lithium ions diffusion in the electrode. Moreover, a capacity of 169 mA h g^{-1} can be resumed when the current density is returned to 50 mA g^{-1} , suggesting the good structural stability of the sample.

4. Conclusions

In summary, introducing FeF_3 aqueous solution into ethanol has been proven to be an effective method for fast preparation of porous FeF_3 nanospheres. It suggests such nanospheres as cathode materials exhibit good rate capability and cycling performance, which could be attributed to their porous structure facilitating electrolyte transport and small particle size shortening electronic and ionic pathways within the electrode. Our present study is important because it provides us a facile approach for rapid production of porous FeF_3 nanospheres for LIBs application.

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